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On Organic Compounds of Arsenic. Part IV. Reaction between the Grignard Reagent and Arsenic Trisulphide.

By

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ABSTRACT

The actions of arsenic trisulphide on phenylmagnesium bromide, α -naphthylmagnesium bromide and p-tolylmagnesium bromide were studied. An interesting fact observed is that arsenic trisulphide acts upon p-tolylmagnesium bromide in two different ways according to the mode of the preparation. When arsenic trisulphide precipitated by hydrogen sulphide in an acid solution and subsequently dried at 100° was used, tri-p-tolylarsine sulphide and di-p-tolylarsine sulphide were produced with a small quantity of tri-p-tolylarsine, while arsenic trisulphide precipitated by hydrogen sulphide and subsequently treated with carbon dioxide to drive off the excess of hydrogen sulphide, washed with carbon bisulphide and then dried at 100°, gave tri-p-tolylarsine and di-p-tolylarsine sulphide but not tri-p-tolylarsine sulphide.

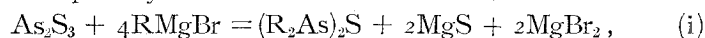
Di- α -naphthylarsine sulphide was obtained in the form of colourless crystals, m. p. 185–186°. It was also prepared from di- α -naphthylarsine oxide or di- α -naphthylchloroarsine by the action of hydrogen sulphide, and was transformed to di- α -naphthylarsinic acid by treating it with chlorine. $2[(C_{10}H_7)_2As]_2S + 7 Cl_2 = 4(C_{10}H_7)_2AsCl_3 + S_2Cl_2, (C_{10}H_7)_2AsCl_3 + 2H_2O = (C_{10}H_7)_2AsO_2H + 3HCl$. The formation of sulphur monochloride in this reaction was easily recognized by its characteristic smell.

Triphenylarsine sulphide mercurichloride, $(C_6H_5)_3AsS \cdot HgCl_2$, m. p. 239–241°, tri-p-tolylarsine sulphide mercurichloride, $(C_7H_7)_3AsS \cdot HgCl_2$, m. p. 227–229°, were prepared and their properties were recorded.

From the study of the action of arsenic trisulphide on the Grignard reagent the interesting fact was found that the mode of its preparation has a great influence upon the reaction. Finely powdered arsenic trisulphide and phenylmagnesium bromide reacted energetically and gave triphenylarsine sulphide and triphenylarsine when the reaction product was treated with water and dilute acetic acid. Diphenylarsine sulphide, which is rather

difficult to crystallize, was identified by transforming it into diphenylarsinic acid. The reaction between p-tolylmagnesium bromide and arsenic trisulphide smoothly set in and produced tri-p-tolylarsine sulphide with an oily product, which could easily be oxidized into di-p-tolylarsinic acid. By the reaction between α -naphthylmagnesium bromide and arsenic trisulphide, di- α -naphthylarsine sulphide was only produced.

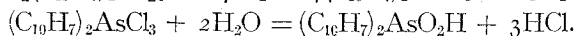
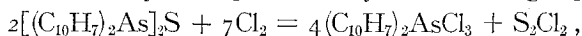
From the above experiments, it will be noticed that arsenic trisulphide reacts upon the Grignard reagent just in a way analogous to the action of the trioxide¹ and produces the secondary and tertiary arsine compounds, but not the primary thus :



In the case of α -naphthylmagnesium bromide, the reaction comes to a stop at the stage of equation (i), probably because α -naphthylmagnesium bromide does not react on di- α -naphthylarsine sulphide so as to change the latter into the tertiary compound. To confirm whether the reaction (ii) actually takes place, diphenylarsine sulphide prepared by treating the corresponding arsine oxide with hydrogen sulphide, was treated with phenylmagnesium bromide. As was expected, triphenylarsine was obtained as the only reaction product, triphenylarsine sulphide not being produced.

The formation of diarylarsinic acid by oxidation of diarylarsine sulphide was confirmed by experiment as was described in the experimental part of this memoir.

The reaction may be represented by the following equations.



As to the formation of triphenylarsine sulphide and tri-p-tolylarsine sulphide a doubt naturally arises that they may be the products of reactions of triarylarsines upon sulphur which may have existed as an impurity in the arsenic trisulphide, for those tertiary arsines are generally very active towards sulphur and combine with it without difficulty².

To make this ambiguous point clear several experiments were performed arsenic trisulphide prepared in four different ways being used.

I. The precipitates formed in a warm hydrochloric acid solution by hydrogen sulphide were well washed with hot water containing a small quantity of hydrogen sulphide and dried in a desiccator and then at 100° in an air bath.

¹ K. Matsumiya and M. Nakai, These Memoirs, **8**, 307 (1925).

² La Coste and Michaelis, Lieb. Ann., **201**, 244 (1880); Michaelis, Lieb. Ann., **321**, 204 (1902).

II. After the precipitates were dried as above, they were washed in a Soxlet tube with carbon bisulphide and then dried at 100° .

III. The precipitates together with the mother liquor were treated with carbon dioxide gas so as to expel hydrogen sulphide completely. Then they were well washed with warm water containing a small quantity of hydrogen sulphide, dried in a desiccator and finally heated at 100° in an air bath.

IV. The precipitates prepared in the manner described in III were washed with carbon bisulphide in a Soxlet tube and dried in an air bath at 100° .

All these arsenic trisulphides readily acted upon p-tolylmagnesium bromide, but the reaction products differed in each case.

Sulphide (I) The main product was tri-p-tolylarsine sulphide, together with a small quantity of tri-p-tolylarsine and di-p-tolylarsine sulphide.

Sulphide (II) Tri-p-tolylarsine was chiefly produced. A small quantity of tri-p-tolylarsine sulphide and di-p-tolylarsine sulphide was also produced.

Sulphide (III) and (IV) Tri-p-tolylarsine and di-p-tolylarsine sulphide were formed, but no tri-p-tolylarsine sulphide.

According to the investigation of O. Puller,¹ arsenic trisulphide prepared by method (I) contains about 2 % more sulphur than the theory demands, and the above experiment shows that the more free sulphur is washed away the less tri-p-tolylarsine sulphide is formed. These facts seem at first sight to show that the formation of tri-p-tolylarsine sulphide is due to the action of sulphur. Nevertheless, the quantity of tri-p-tolylarsine sulphide produced was rather great to be regarded as having been formed by the action of sulphur contained as an impurity. No such different reactions with arsenic trisulphide could be observed in the case of phenylmagnesium bromide, triphenylarsinesulphide being found almost in the same quantity in every case. Accordingly the presence of sulphur as an impurity was seen to have no influence upon the resulting product.

EXPERIMENTAL PART.

1. *Action of Phenylmagnesium Bromide upon Arsenic Trisulphide.*

To the Grignard reagent prepared from 15.7 gram. ($1/10$ mol.) of bromobenzene, 2.5 gram. ($1/10$ mol.) of magnesium and a trace of methyl

¹ Z. Anal. Chem., **10**, 41 (1871).

iodide in 30 c.c of dry ether, 6.2 gm. ($1/40$ mol.) of powdered arsenic trisulphide were gradually added. A vigorous reaction took place accompanied by heat generation. When the reaction subsided, the reaction product was boiled for an hour in a water-bath. After standing over night, the product was decomposed with water and then with dilute acetic acid and distilled with steam to drive off ether and diphenyl. The residue was extracted with ether and the ethereal solution was dried with anhydrous sodium sulphate and evaporated when a residue solidifying gradually on standing was obtained. It was washed with ether to remove a yellow oily substance adhering and recrystallized from alcohol. Colourless needles melting at $161-162^{\circ}$ were obtained. The yield was 2.3 gm. The analyses for arsenic and sulphur gave the following values.

0.2521 gm. of the sample gave 0.1716 gm. BaSO_4 .

0.2487 gm. substance required 29.4 c.c of N/20 iodine solution.

	Calc. for $(\text{C}_6\text{H}_5)_3\text{AsS}$	Found
As	22.17	22.16
S	9.45	9.35

The ethereal washing was concentrated and kept in vacuo for many days, and the crystals thus separated were pressed between filter-papers to remove a yellow oily substance and recrystallized from ether. About 2.2 gm. of colourless crystals melting at $58-60^{\circ}$ were obtained. They were analysed with the following result:—

0.1368 gm. substance required 17.82 c.c of N/20 iodine solution.

	Calc. for $(\text{C}_6\text{H}_5)_3\text{As}$	Found
As	24.49	24.42

The yellow oily substance absorbed in filter-papers was extracted with ether and treated with an ethereal solution of mercuric chloride when white crystalline precipitates were instantly formed. The precipitates were dissolved in boiling alcohol and into the solution hydrogen sulphide was passed. The filtered solution, on concentration, gave fine needles which were washed with a small quantity of ether and recrystallized from alcohol. The colourless needles (yield, 0.2 gm.) thus formed melted at $161-162^{\circ}$. They were identified as triphenylarsine sulphide.

On evaporating the ethereal washing, an oily residue solidifying gradually on standing was left. After removal of yellow oily impurities, the residue was recrystallized from ether several times, and colourless crystals melting at $58-60^{\circ}$ were finally obtained. The yield was 0.7 gm. They

1 Philips, Ber. D. Chem. Ges., **19**, 1032 (1886); La Coste and Michaelis, loc. cit

were proved to be triphenylarsine on their properties being examined.

The ethereal solution containing mercuric chloride was repeatedly washed with dilute hydrochloric acid and then saturated with chlorine. After the evaporation of ether, the residue was treated with a dilute caustic soda solution and decolourized with animal charcoal. On acidifying the solution with hydrochloric acid, white precipitates were produced. When recrystallized from hot water 0.5 gm. of colourless crystals melting at $170-171^{\circ}$ ¹ was obtained. Its analytical result was as follows:—

0.1415 gm. substance required 21.53 c.c of N/20 iodine solution.

	Calc. for $(C_6H_5)_2AsO.OH$	Found
As	28.61	28.53

In the above reactions, all sorts of arsenic trisulphide were seen to give nearly the same result.

2. Action of *p*-Tolylmagnesium Bromide upon Arsenic Trisulphide².

a) The trisulphide prepared by method (I) was used.

The ethereal solution of *p*-tolylmagnesium bromide prepared from 9 gm. (1/20 mol.) of *p*-bromotoluene, 1.3 gm. (1/20 mol.) of magnesium and a trace of methyl iodide in 30 c.c of dry ether was treated slowly with 3.1 gm. (1/80 mol.) of arsenic trisulphide, and then the mixture was boiled for an hour in a water-bath. The product was decomposed with water and dilute acetic acid and subjected to steam distillation to remove ether and di-*p*-tolyl. The residue was extracted with ether and the ethereal solution was dried with sodium sulphate. After removal of ether, a viscid oil crystallizing on standing was obtained. The solidified mass was pressed between filter-papers to remove a yellowish oily substance and washed with a small quantity of alcohol. By several fractional crystallizations from alcohol, 0.8 gm. of colourless fine needles melting at $166-167^{\circ}$ ³ and 0.2 gm. of colourless rhombic crystals melting at $146-147^{\circ}$ ⁴ were isolated. The analyses gave the following results.

0.1623 gm. of the needle crystals required 17.1 c.c of N/20 iodine solution.

¹ K. Matsuniya and M. Nakai, loc. cit., 311; La Coste and Michaelis, loc. cit., 271,

² In these experiments, we used four specimens of arsenic trisulphide prepared by different methods as described before..

³ Michaelis, loc. cit.

⁴ K. Matsuniya and M. Nakai, loc. cit., 312; La Coste, Lieb. Ann., **208**, 26 (1881); Michaelis, loc. cit., 200.

0.25111 gm. substance gave 0.1550 gm. BaSO_4 .

	Calc. for $(\text{CH}_3 \cdot \text{C}_6\text{H}_4)_3\text{AsS}$	Found
As	19.72	19.75
S	8.43	8.47

0.1443 gm. of the rhombic crystals required 16.55 c.c of N/20 iodine solution.

	Calc. for $(\text{CH}_3 \cdot \text{C}_6\text{H}_4)_3\text{As}$	Found
As	21.53	21.50

The oily substance was dissolved in ether and treated with an ethereal solution of mercuric chloride. The mercurichloride then formed was dissolved in boiling alcohol and then saturated with hydrogen sulphide to remove mercury as mercuric sulphide. On concentration, the filtered alcoholic solution gave 0.2 gm. of needle crystals together with a small quantity of rhombic crystals.

The ethereal solution containing the excess of mercuric chloride was well washed with dilute hydrochloric acid and treated with chlorine. Then it was extracted with a dilute caustic soda solution and decolourized with animal charcoal; on acidifying it with hydrochloric acid, colourless crystals crystallizing in fine needles from hot water were obtained. It melted at $173-174^\circ$. The yield was 0.4 gm. The analytical result was as follows:-

0.1418 gm. substance required 19.25 c.c of N/20 iodine solution.

	Calc. for $(\text{CH}_3 \cdot \text{C}_6\text{H}_4)_2\text{AsO} \cdot \text{OH}$	Found
As	25.84	25.46

b) The trisulphide prepared by method (II) was used.

Experiments were carried out under the same conditions as above, and as main products, 1.2 gm. of tertiary arsine and 0.2 gm. of tertiary arsine sulphide were obtained. From the mercurichloride 0.2 gm. of tertiary arsine accompanied by a small amount of tertiary arsine sulphide was obtained, and from the oily substance, 0.1 gm. of secondary arsinic acid.

c) The trisulphide prepared by method (III) or (IV) was used.

As the products, 2.2 gm. of tertiary arsine, 0.2 gm. of the same arsine from its mercurichloride and 0.1 gm. of secondary arsinic acid from the oily substance were obtained. Tertiary arsine sulphide was never produced in this case.

3. Action of α -Naphthylmagnesium Bromide upon Arsenic Trisulphide.

To the ethereal solution of α -naphthylmagnesium bromide prepared

1 K. Matsumiya and M. Nakai, loc. cit.; La Coste, loc. cit., 20.

from 20.7 gm. (1/10 mol.) of α -bromonaphthalene, 2.5 gm. (1/10 mol.) of magnesium and a piece of iodine in 60 c.c of dry ether, 6.2 gm. (1/40 mol.) of arsenic trisulphide were added little by little and then the mixture was boiled for an hour on a water-bath. It was decomposed with water and dilute acetic acid and subjected to steam distillation to remove ether and naphthalene. The residue was extracted with chloroform, and on concentrating this chloroform solution a yellowish solid was obtained. It was extracted with ether in a Soxhlet tube to remove coloured impurities when a pale yellow powder was left in the apparatus. It was recrystallized several times from chloroform, and colourless crystals were obtained whose melting point was 185–186°. The yield was 7.2 gm. It was analyzed and gave the following results:—

0.1640 gm. substance gave 0.4184 gm. CO_2 and 0.0630 gm. H_2O .

0.1608 gm. substance required 18.55 c.c of N/20 iodine solution.

0.5670 gm. substance gave 0.1866 gm. BaSO_4 .

	Calc. for $[(\text{C}_{10}\text{H}_7)_2\text{As}]_2\text{S}$	Found
As	21.72	21.64
C	69.54	69.58
H	3.99	4.30
S	4.64	4.52

Di- α -naphthylarsine sulphide is insoluble in ether and alcohol, soluble in benzene and more easily so in hot benzene, carbon bisulphide and chloroform.

4. Action of Phenylmagnesium Bromide upon Diphenylarsine Sulphide.

The Grignard reagent prepared from 4 gm. (1/40 mol.) of bromobenzene, 0.7 gm. (1/40 mol.) of magnesium and a trace of methyl iodide in 30 c.c of dry ether was treated with 2.5 gm. (1/200 mol.) of diphenylarsine sulphide, and then the mixture was boiled for five hours on a water-bath. On cooling, the reaction product was decomposed with water and dilute acetic acid, and ether and diphenyl were distilled off with steam. The residue was extracted with ether and the extract was dried with sodium sulphate. On concentrating the solution, a yellow viscid oil was obtained which solidified on standing. The crystals were separated from oily matter by pressing between filter-papers and recrystallized from ether repeatedly. 1.8 gm. of colourless crystals melting at 58–60° were obtained. They were analyzed with the following result.

0.1515 gm. substance required 19.85 c.c of N/20 iodine solution.

	Calc. for $(C_6H_5)_3As$	Found
As	24.49	24.57

The oily matter was dissolved in ether and treated with an ethereal solution of mercuric chloride, whereby white precipitates were instantly formed. From this mercurichloride, 0.5 gm. of triphenylarsine was obtained by treating it with alcoholic potash. No triphenylarsine sulphide was obtained.

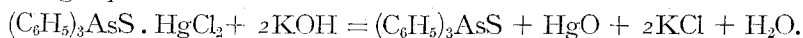
5. Formation of Triphenylarsine Sulphide Mercurichloride.

On adding the ethereal solution of mercuric chloride to triphenylarsine sulphide in an alcoholic medium, a white crystalline powder was instantly precipitated. It was recrystallized from hot absolute alcohol, and colourless crystals melting at $239-241^\circ$ were obtained.

Mercury was estimated as follows:— The substance was dissolved in hot absolute alcohol and then saturated with hydrogen sulphide. The black mercuric sulphide produced was collected in a Gooch crucible, washed with alcohol and water, dried at 105° and weighed. By this method 0.1677 gm. of the sample gave 0.0638 gm. HgS.

	Calc. for $(C_6H_5)_3AsS \cdot HgCl_2$	Found
Hg	32.91	32.80

Triphenylarsine sulphide mercurichloride is soluble in hot absolute alcohol, less so in dilute spirit and insoluble in ether and water. It was unaffected by cold aqueous caustic potash, but when heated it gave triphenylarsine sulphide liberating mercury as mercuric oxide according to the following equation.



When treated with cold alcoholic potash, it also yielded triphenylarsine sulphide. It was also decomposed by hydrogen sulphide in hot alcoholic solution, and gave triphenylarsine sulphide.

6. Formation of Tri-p-tolylarsine Sulphide Mercurichloride.

The ethereal solution of mercuric chloride was added to tri-p-tolylarsine sulphide in the same medium, whereby white crystalline powder was produced. After several recrystallizations from hot alcohol colourless crystals melting at $227-229^\circ$ were obtained. Analysis gave the following result:—

0.1409 gm. substance gave 0.0501 gm. HgS.

	Calc. for $(C_7H_7)_3AsS \cdot HgCl_2$	Found
Hg	30.77	30.66

Tri-p-tolylarsine sulphide mercurichloride is easily soluble in hot absolute alcohol and insoluble in ether and water. On heating with aqueous caustic

potash or treating with cold alcoholic potash or with hydrogen sulphide in an alcoholic medium it gave tri-p-tolylarsine sulphide.

7. *Action of Hydrogen Sulphide upon Di- α -naphthylarsine Oxide.*

Carbon bisulphide solution of di- α -naphthylarsine oxide was saturated with hydrogen sulphide and after removal of the solvent the residue was extracted with ether in a Soxlet tube. A slightly yellow coloured powder was left behind which, when recrystallized from chloroform, formed colourless crystals melting at 185–186°. Its analytical result for arsenic was as follows:—

0.1552 grm. substance required 17.82 c.c of N/20 iodine solution.

	Calc. for $[(C_{10}H_7)_2As]_2S$	Found
As	21.72	21.53

8. *Action of Hydrogen Sulphide upon Di- α -naphthylchloroarsine.*

Dry hydrogen sulphide was passed into a benzene-alcoholic solution of di- α -naphthylchloroarsine. On evaporating the solvent a brownish residue was obtained which was then washed with ether in a Soxlet apparatus. After several recrystallizations from chloroform it was transformed into crystals melting at 185–186°.

0.1537 grm. substance required 17.7 c.c of N/20 iodine solution.

	Calc. for $[(C_{10}H_7)_2As]_2S$	Found
As	21.72	21.59

9. *Action of Chlorine upon Di- α -naphthylarsine Sulphide.*

Dry ether in which di- α -naphthylarsine sulphide was suspended was saturated with dry chlorine, whereby yellow precipitates were instantly formed. Ether was decanted off and the precipitates were washed well with absolute ether to remove the sulphur monochloride formed, and dried by passing dry air over it. It was analyzed after having been kept in vacuo over sulphuric acid.

0.1587 grm. of the sample required 14.45 c.c of N/20 iodine solution.

0.1508 grm. substance gave 0.1454 grm. AgCl.

	Calc. for $(C_{10}H_7)_2AsCl_3$	Found
As	17.22	17.07
Cl	24.43	23.86

Thus di- α -naphthylarsine sulphide was converted into di- α -naphthylarsine trichloride¹ and sulphur monochloride, the latter of which was recognized

¹ K. Matsumiya and M. Nakai, loc. cit., 316.

by its characteristic odour.

10. *Direct Formation of Di- α -naphthylarsinic Acid from
Di- α -naphthylarsine Sulphide*

A mixture of ether and water in which di- α -naphthylarsine sulphide was suspended was saturated with chlorine. The reaction product was treated with a dilute caustic soda solution and decolourized with animal charcoal. On acidifying the solution with hydrochloric acid, white precipitates were obtained which after several recrystallizations from benzene-ether solution formed a white amorphous powder melting at $228-229^{\circ}$.¹ Analysis gave the following value for arsenic.

0.1334 gram. substance required 14.72 c.c of N/20 iodine solution.

	Calc. for $(C_{10}H_7)_2AsO \cdot OH$	Found
As	20.70	20.68

¹ K. Matsumiya and M. Nakai, loc. cit.